

Spectroscopic Methods in Organic Chemistry

CHEM-6124, Organic Chemistry (Minor)

Online Lectures (UV-Vis)

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UV-Vis Spectroscopy

Frequency (ν) = 4.0×10^{14} to 8.6×10^{14} Hz (**Vis**)

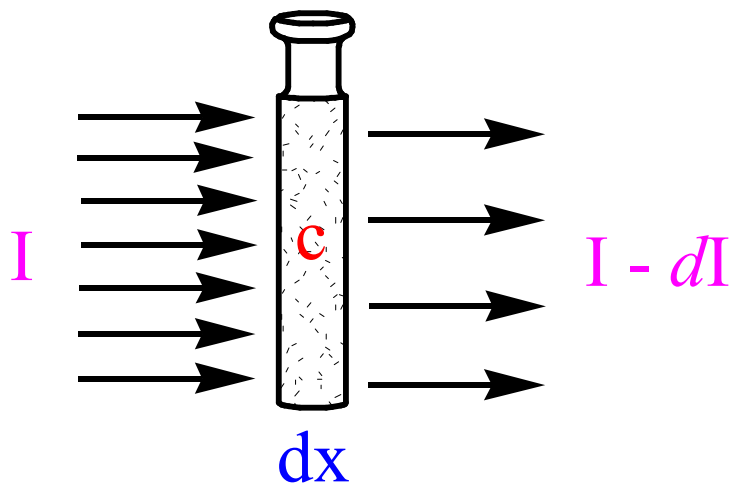
8.6×10^{14} to 1.5×10^{15} Hz (**UV**)

Wavelength (λ) = 750 to 350 nm (**Vis**)

350 to 200 nm (**UV**)

Wave Number ($\tilde{\nu}$) = 1.33×10^6 to 2.9×10^6 m⁻¹ (**Vis**)

2.9×10^6 to 5.0×10^6 m⁻¹ (**UV**)



I = Intensity of EMR

dI = Absorbed EMR

dx / l = Path length

c = Concentration of analyte

Lambert-Beer's Law

$$\left. \begin{array}{l} -dI \propto I \\ -dI \propto c \\ -dI \propto dx \end{array} \right\} \begin{array}{l} -dI \propto I \cdot c \cdot dx \\ -dI = k \cdot I \cdot c \cdot dx \end{array} \quad \Rightarrow \quad \begin{array}{l} \frac{-dI}{I} = k \cdot c \cdot dx \\ \frac{dI}{I} = -k \cdot c \cdot dx \end{array}$$

$$\ln I - \ln I_0 = -k \cdot c \cdot l \quad \Rightarrow \quad \ln \left(\frac{I}{I_0} \right) = -k \cdot c \cdot l$$

$$\log \left(\frac{I}{I_0} \right) = \frac{-k \cdot c \cdot l}{2.303} \quad \Rightarrow \quad \log \left(\frac{I}{I_0} \right) = -\epsilon \cdot c \cdot l$$

$$\left(\frac{I}{I_0} \right) = 10^{-\epsilon c l} \quad \Rightarrow \quad T = 10^{-A}$$

$$A = \epsilon \cdot c \cdot l \quad \epsilon = \frac{A}{c \cdot l} = \frac{1}{\text{mol} / \text{L} \cdot \text{cm}} = \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$$

Absorbance Vs Transmittance

$$T = 10^{-\epsilon c l}$$

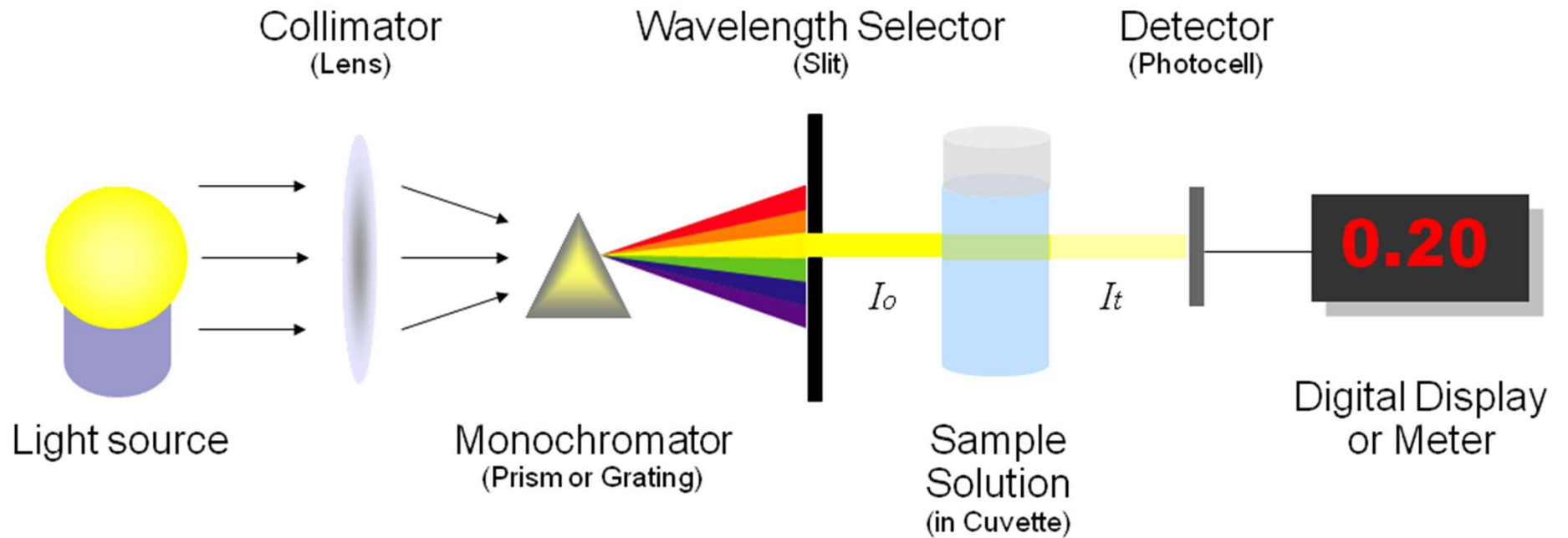
$$\log T = -A$$

$$T = 10^{-A}$$

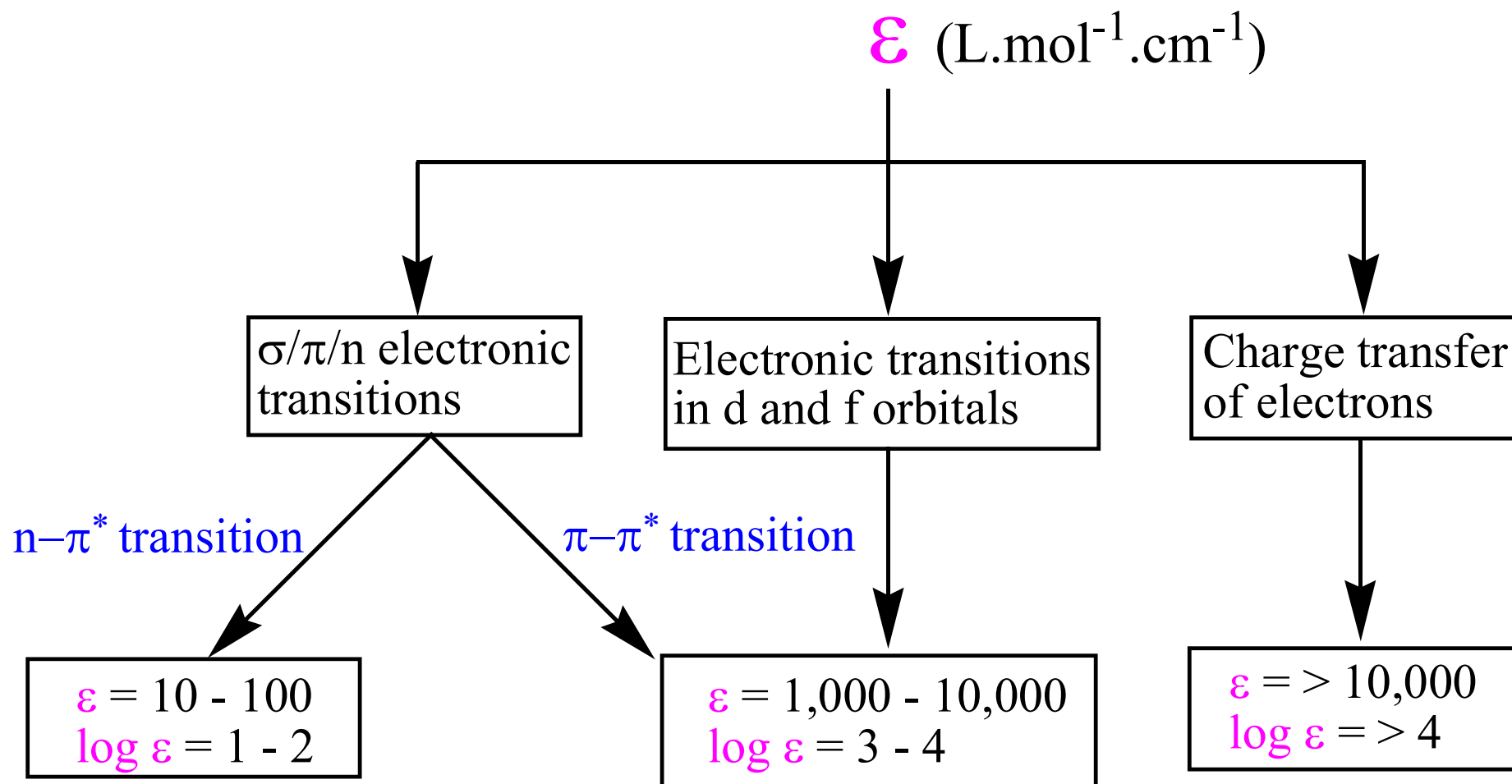
$$A = -\log T$$

A	T	T	A
0.1	0.79	0.1	1
0.2	0.63	0.2	0.70
0.25	0.56	0.25	0.60
0.3	0.50	0.3	0.52
0.4	0.39	0.4	0.40
0.5	0.32	0.5	0.30

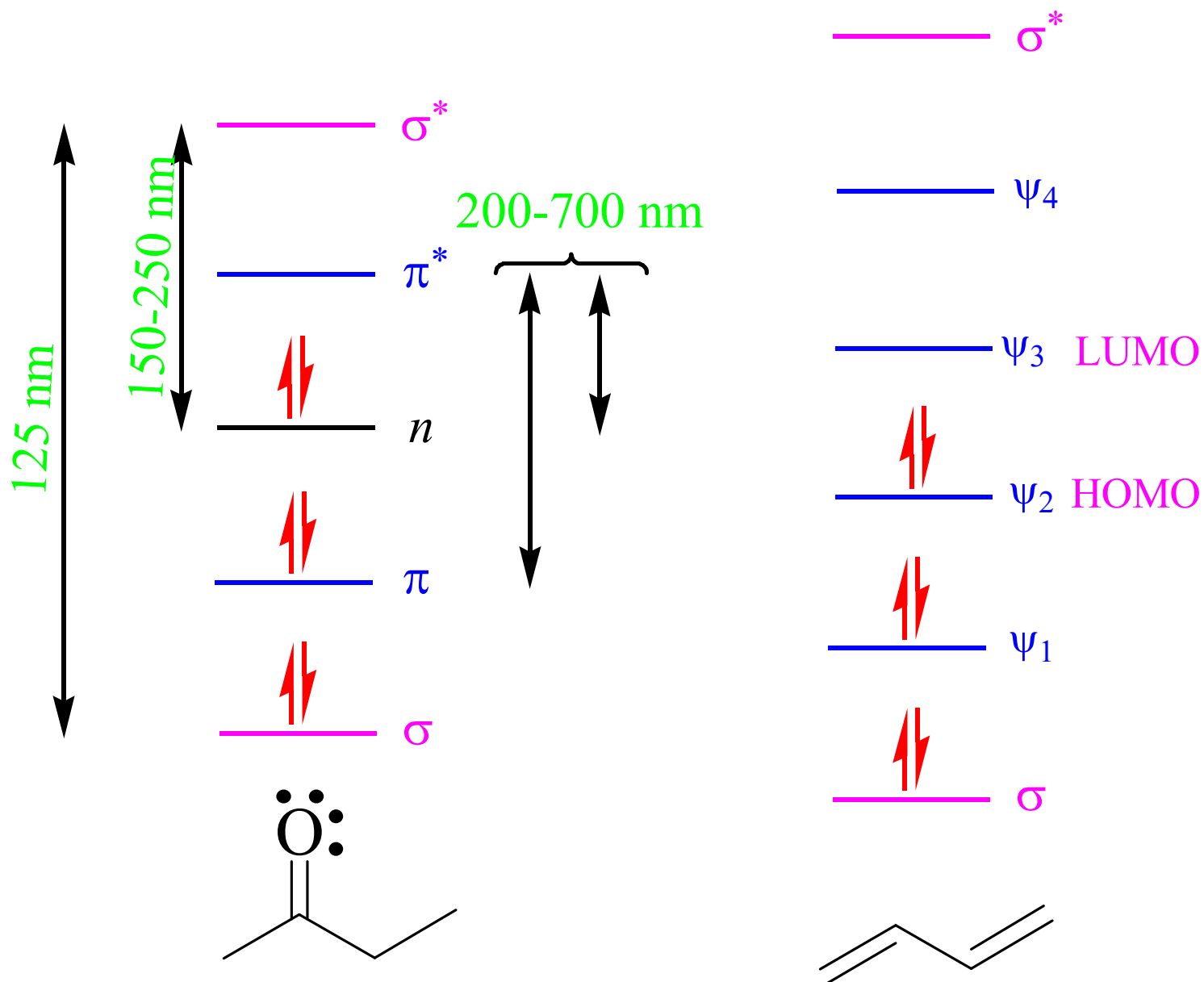
Source of Radiation



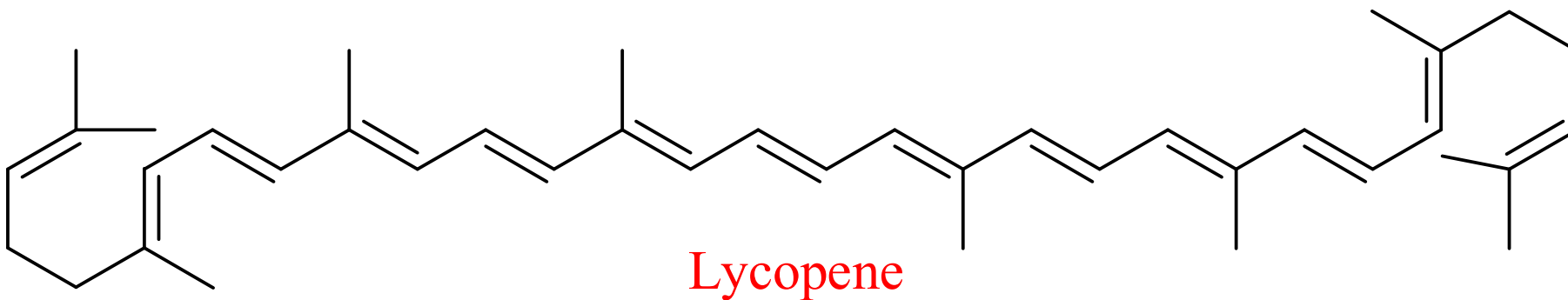
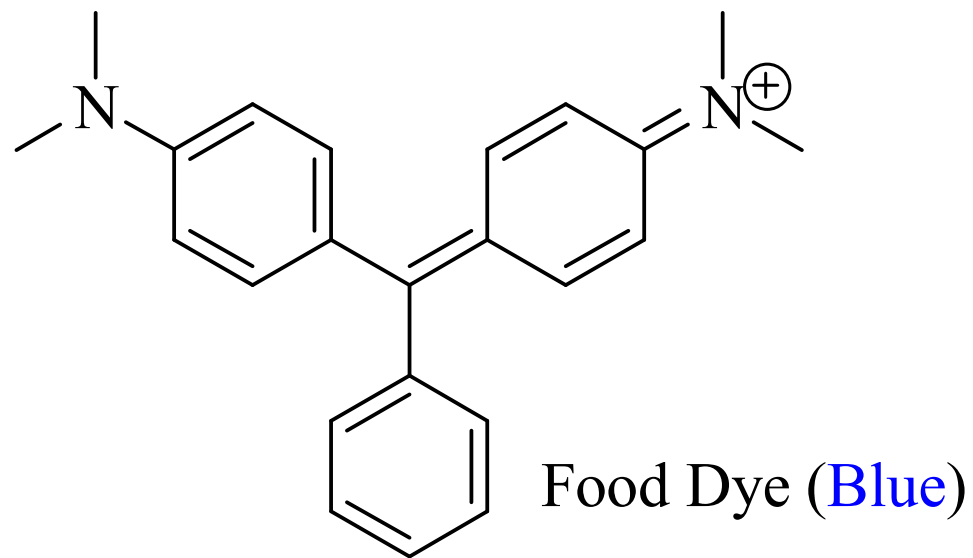
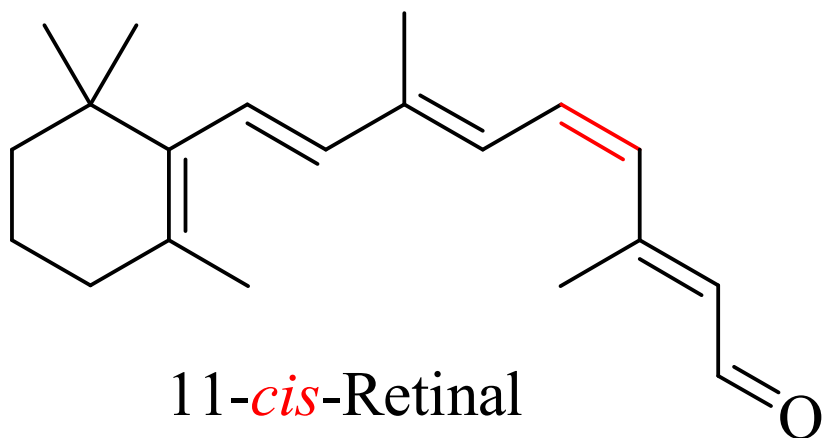
Importance of ϵ



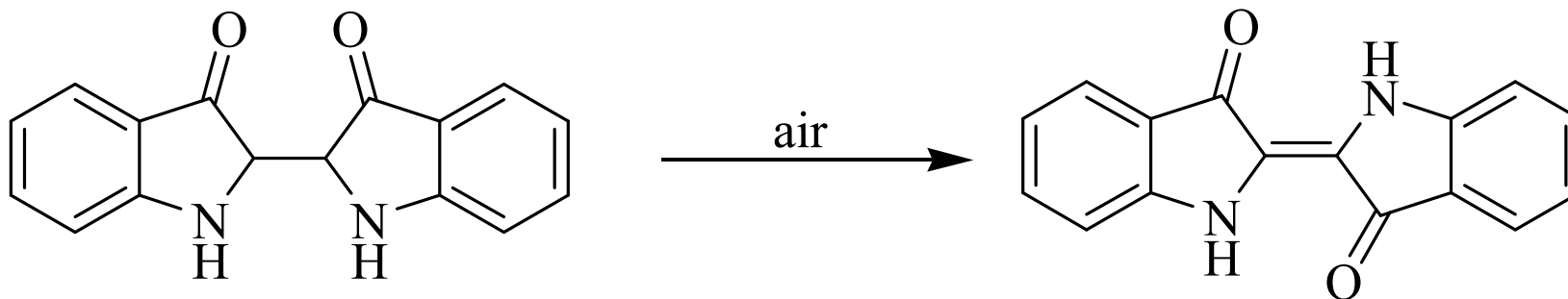
Electronic Transitions $\nu_s \epsilon$



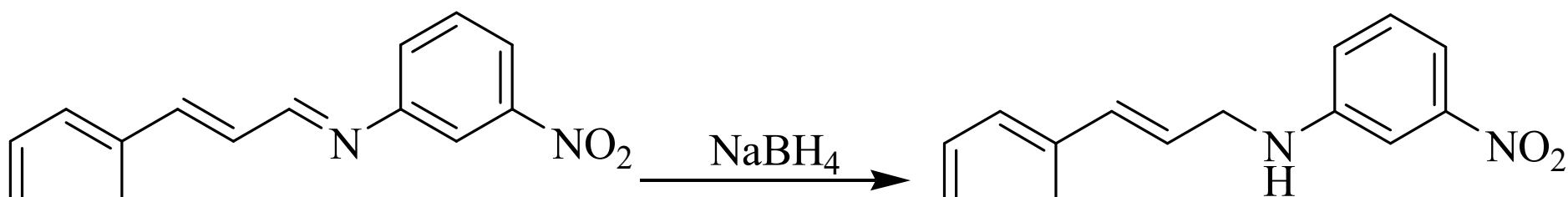
Chromophores



Chromophores



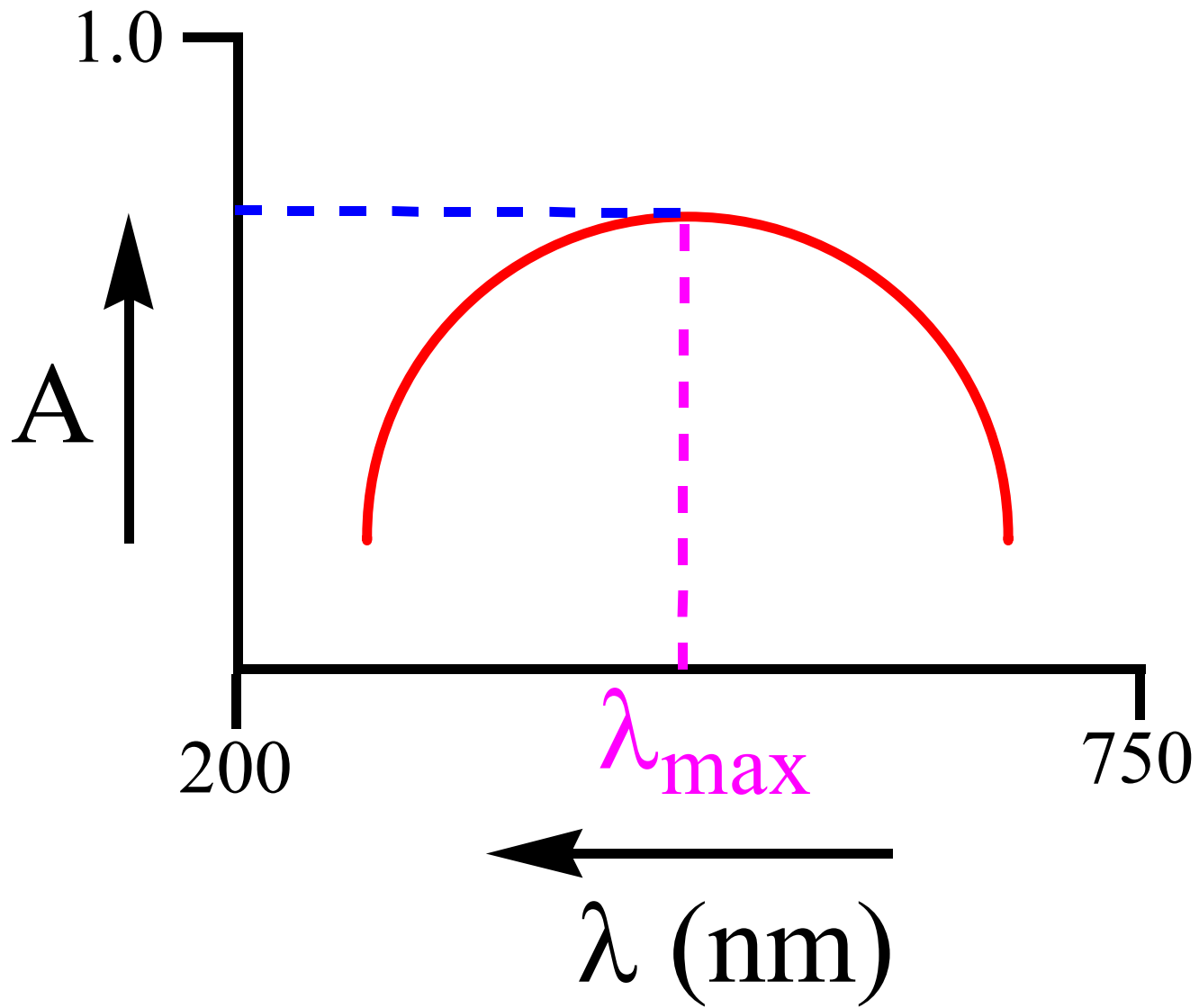
Blue Jeans Dye



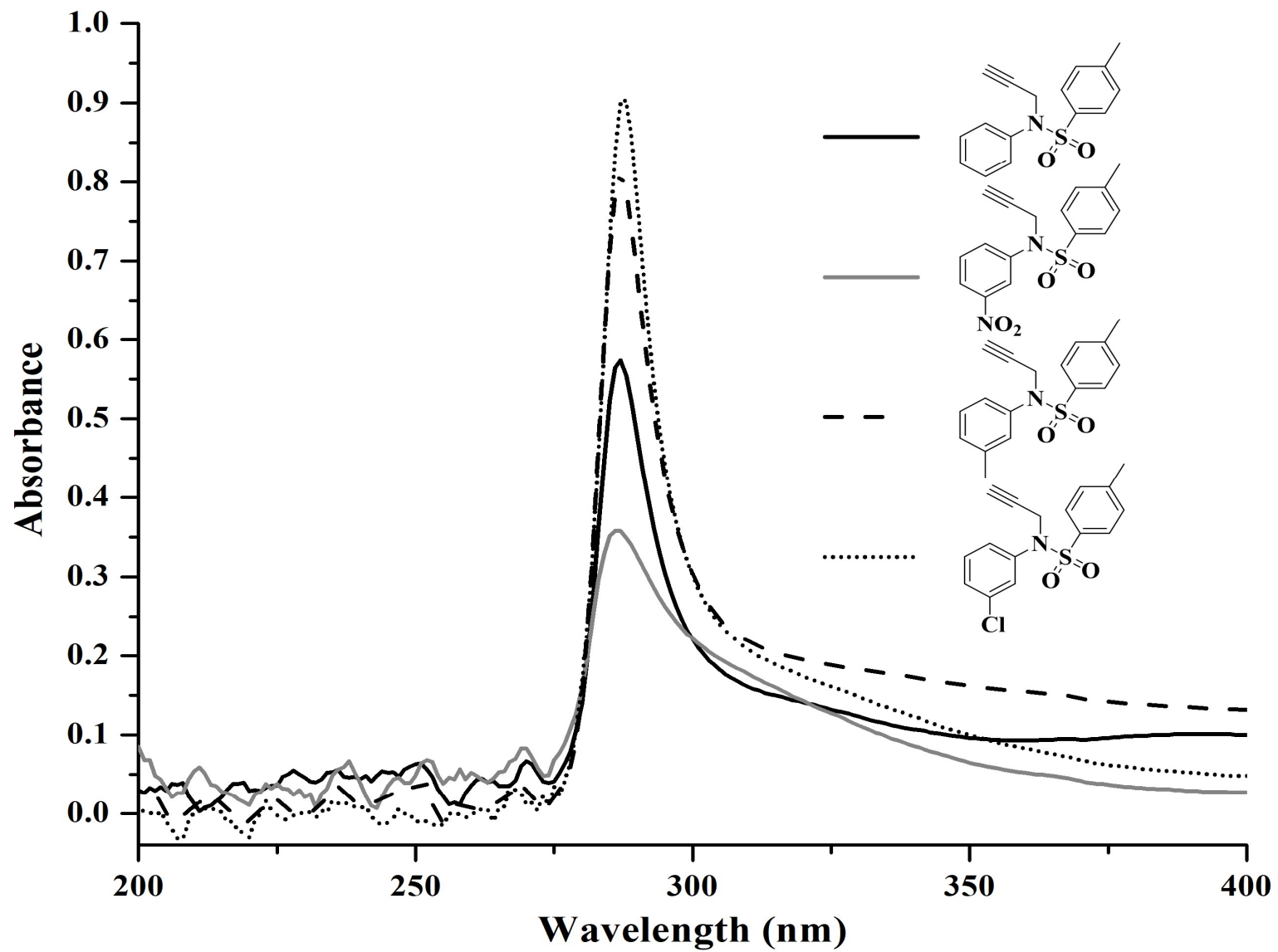
Yellow imine

Colorless amine

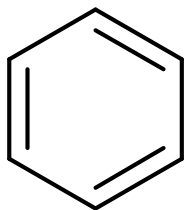
λ_{\max}



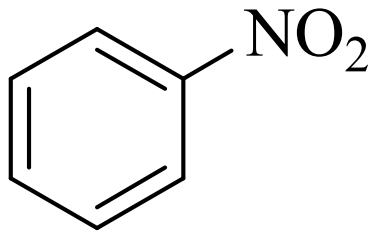
UV Spectra



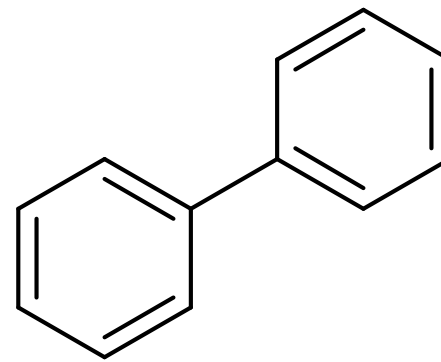
Importance of λ_{\max}



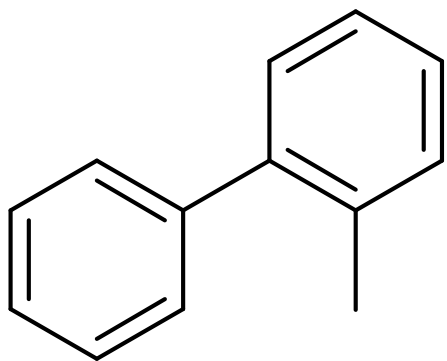
1 $\lambda_{\max} = 203 \text{ nm}$



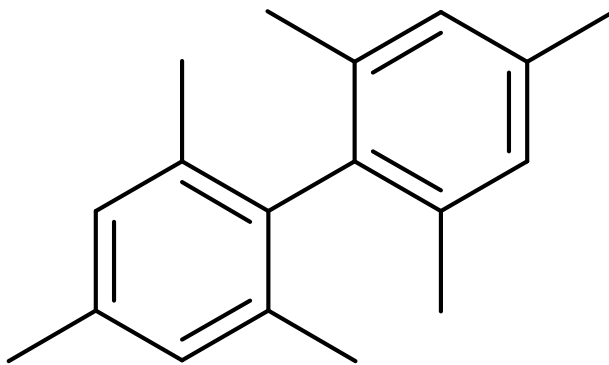
2 $\lambda_{\max} = 268 \text{ nm}$



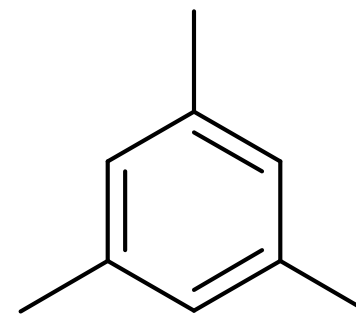
3 $\lambda_{\max} = 250 \text{ nm}$



4 $\lambda_{\max} = 237 \text{ nm}$

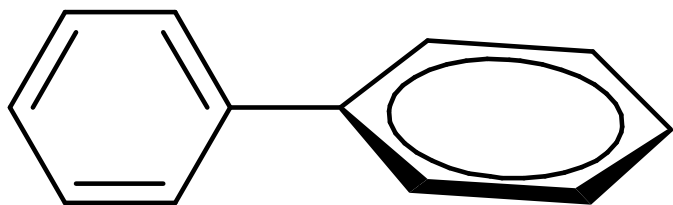


5 $\lambda_{\max} = 266 \text{ nm}$

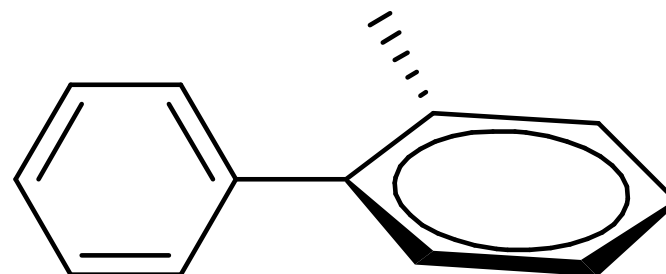


6 $\lambda_{\max} = 266 \text{ nm}$

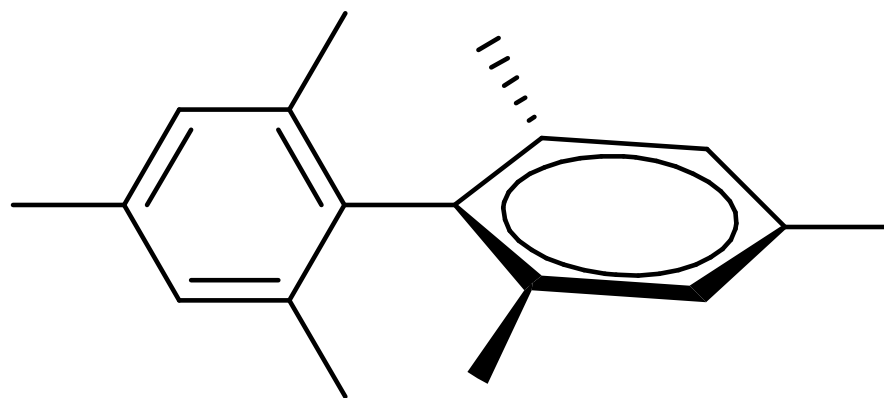
Importance of λ_{\max}



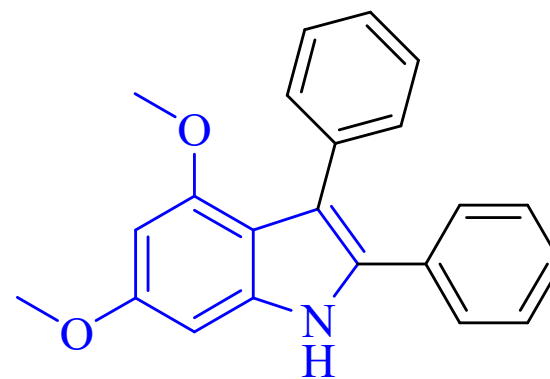
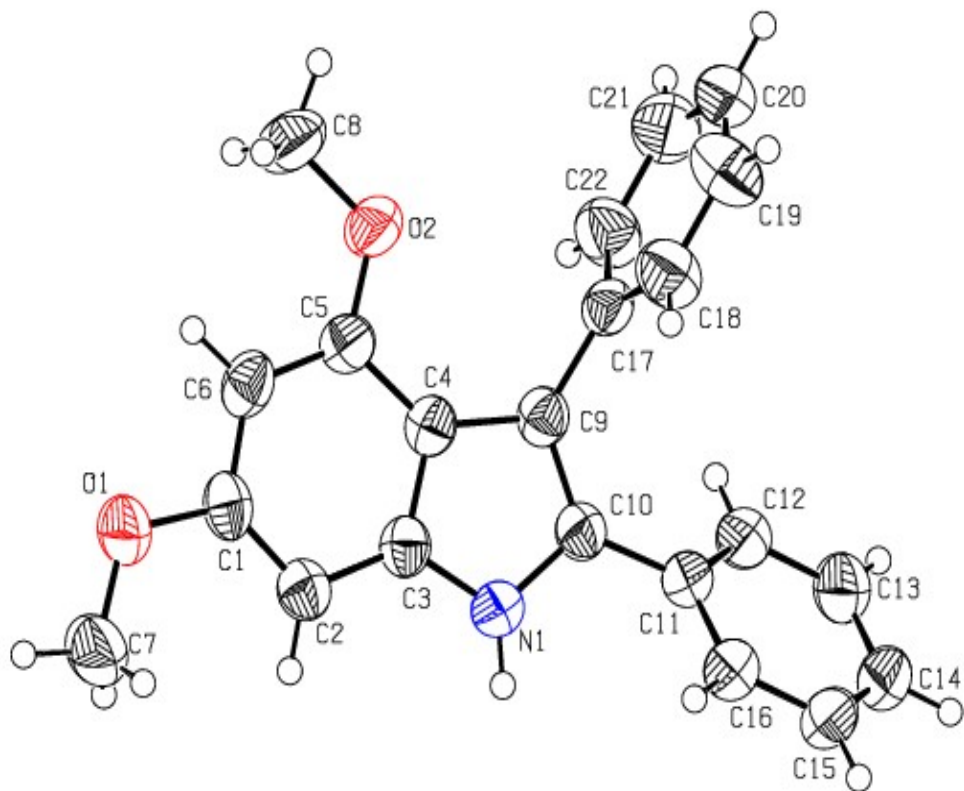
3 $\lambda_{\max} = 250$ nm



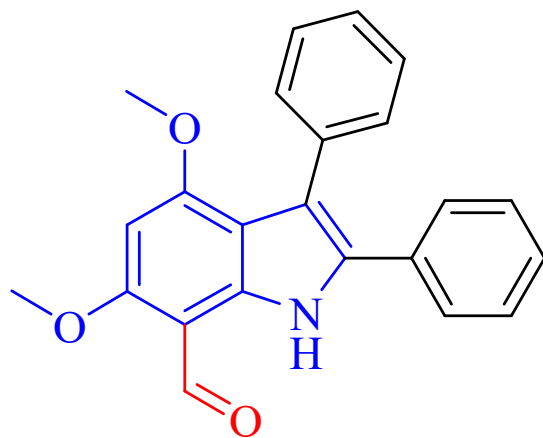
4 $\lambda_{\max} = 237$ nm



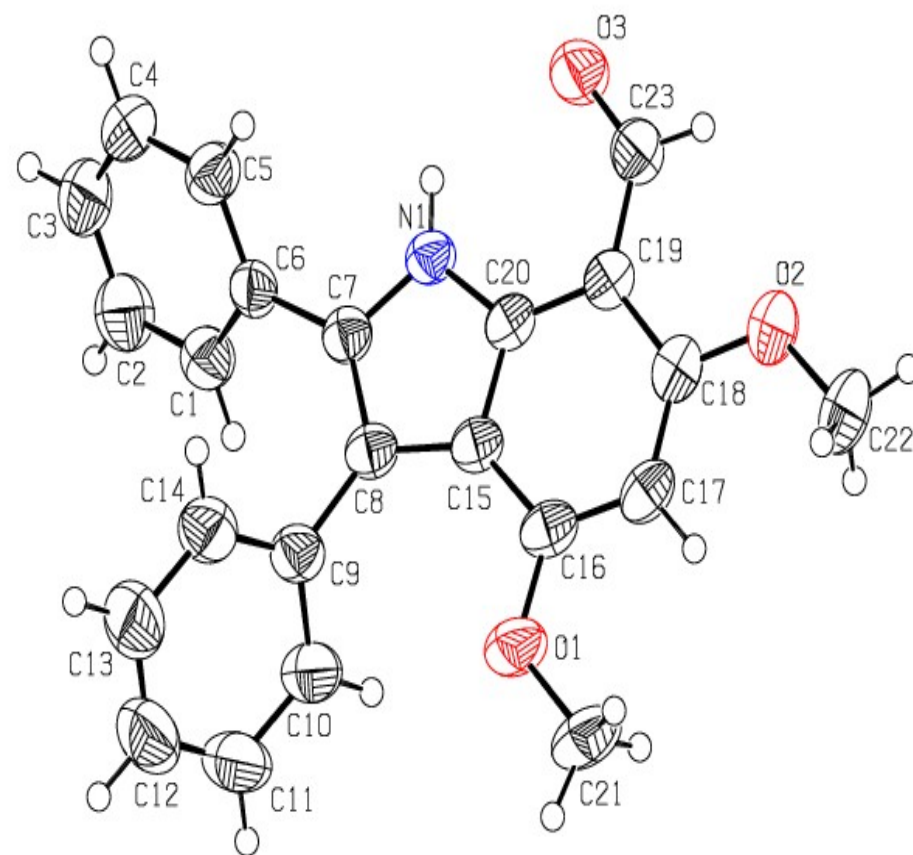
5 $\lambda_{\max} = 266$ nm

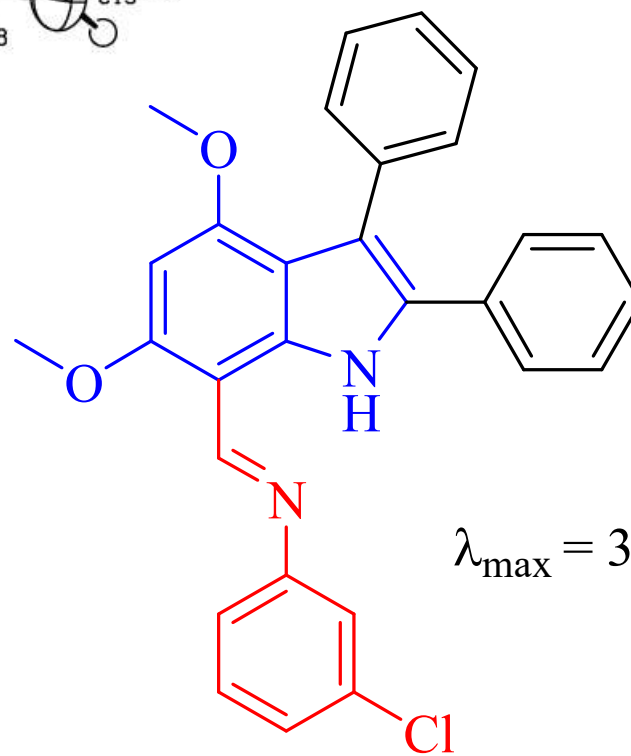
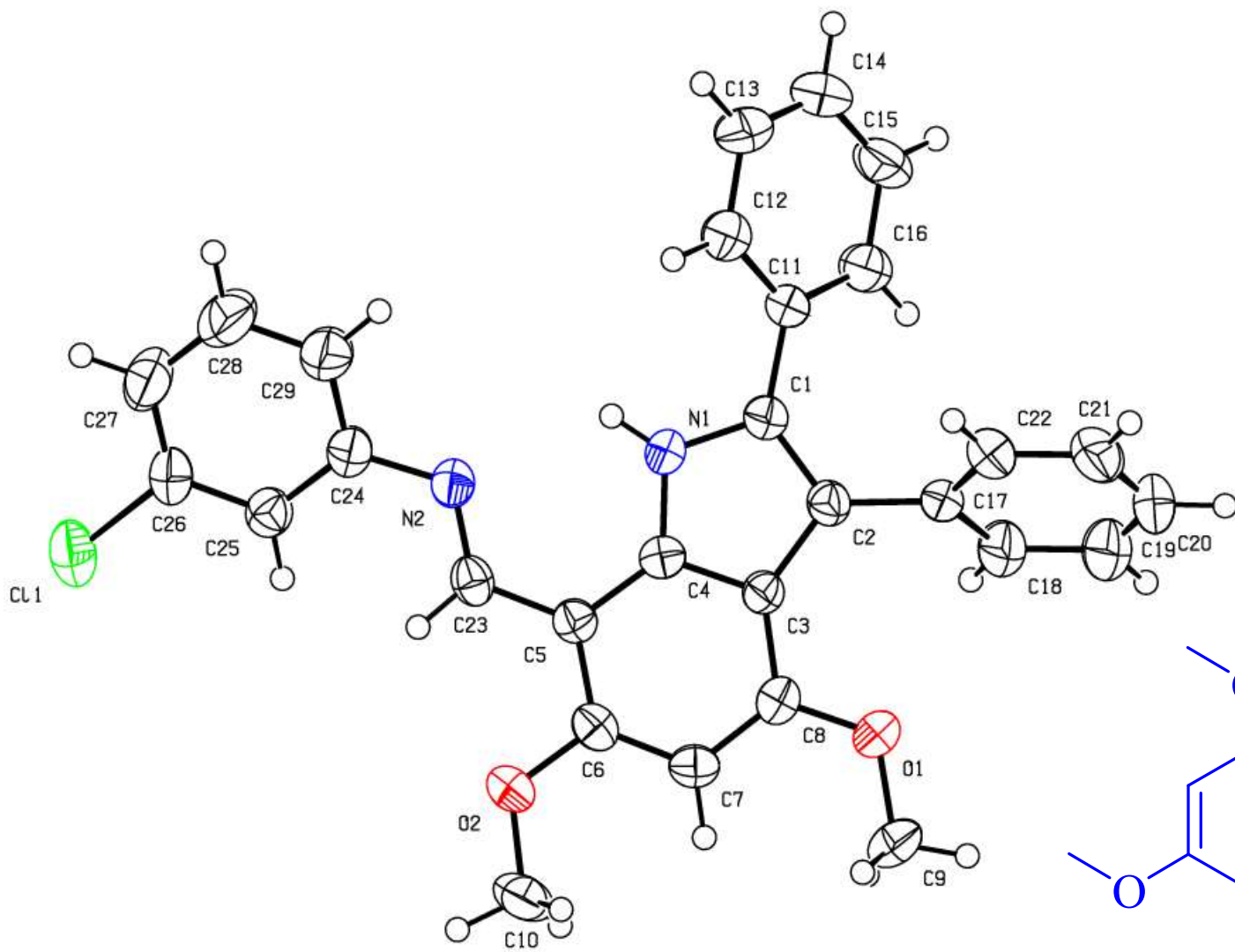


$\lambda_{\text{max}} = 324 \text{ nm}$



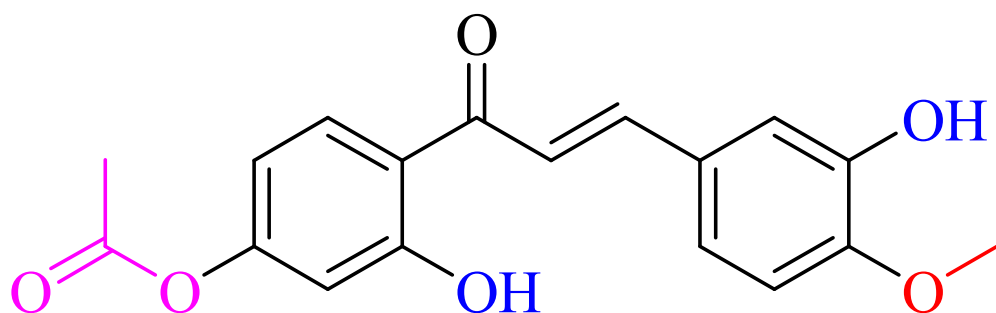
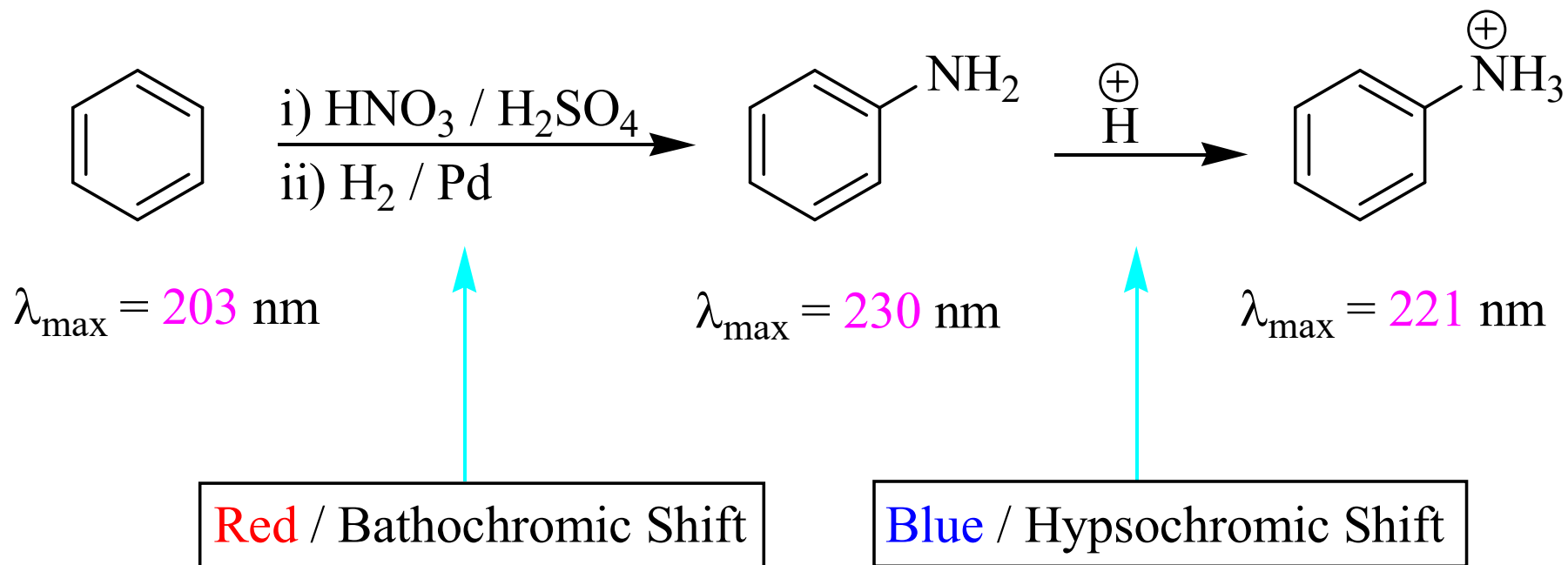
$\lambda_{\text{max}} = 372 \text{ nm}$





$$\lambda_{\max} = 379 \text{ nm}$$

Red / Blue Shifts



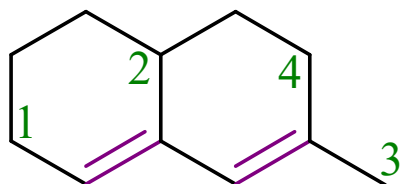
OH, OMe, OAc etc

Auxochromes

Absorbed vs Transmitted Colour

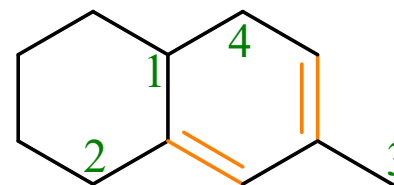
<u>Colour (Absorbed)</u>	<u>Colour (Transmitted)</u>	<u>λ (nm)</u>
UV	-	200-350
Violet	Yellow-Green	350-425
Indigo-Blue	Yellow	425-450
Blue	Orange	450-490
Blue-Green	Red	490-510
Green	Purple	510-530
Yellow-Green	Violet	530-550
Yellow	Indigo-Blue	550-590
Orange	Blue	590-640
Red	Blue-Green	640-720
Purple	Green	720-750

Calculating λ_{\max} (Woodward-Fieser's Rule)



Heteroannular diene (**A**) = 214 nm
 Double bond extension (**C**) = +30 nm
 Exocyclic double bond (**D**) = +5 nm

$$\lambda_{\max} (\text{nm}) = \mathbf{A/B} + \mathbf{C} + \mathbf{D} + \text{Substituents}$$

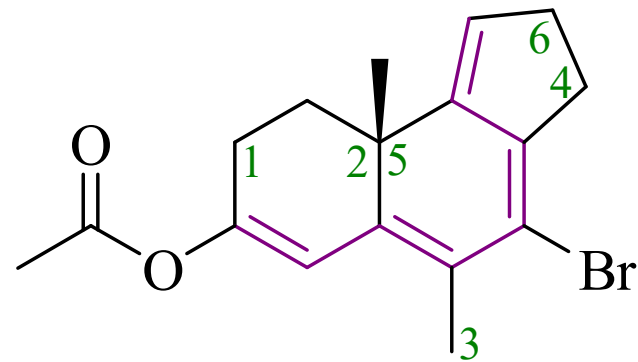
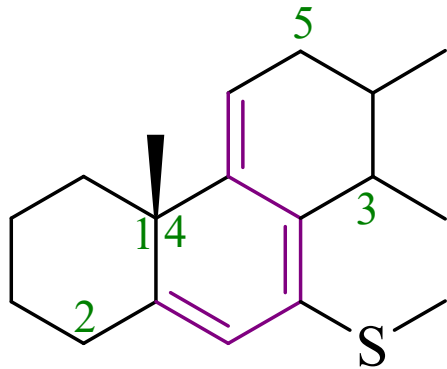


Homoannular diene (**B**) = 253 nm
 Double bond extension (**C**) = +30 nm
 Exocyclic double bond (**D**) = +5 nm

Substituents

Sec. aminic group = +60 nm
 Alkylthio (-SR) group = +30 nm
 Alkoxy (-OR) group = +6 nm
 Halo / alkyl (-R) group = +5 nm
 Acetato (-OCOR) group = 0 nm

Calculating λ_{\max}



$$\lambda_{\max} (\text{nm}) = \mathbf{A/B+C+D+Substituents}$$

$$\lambda_{\max} (\text{nm}) = 253+30+3(5)+[30+5 \times 5]$$

$$\lambda_{\max} (\text{nm}) = \mathbf{353 \text{ nm}}$$

if -SR group is replaced by -NR₂ group

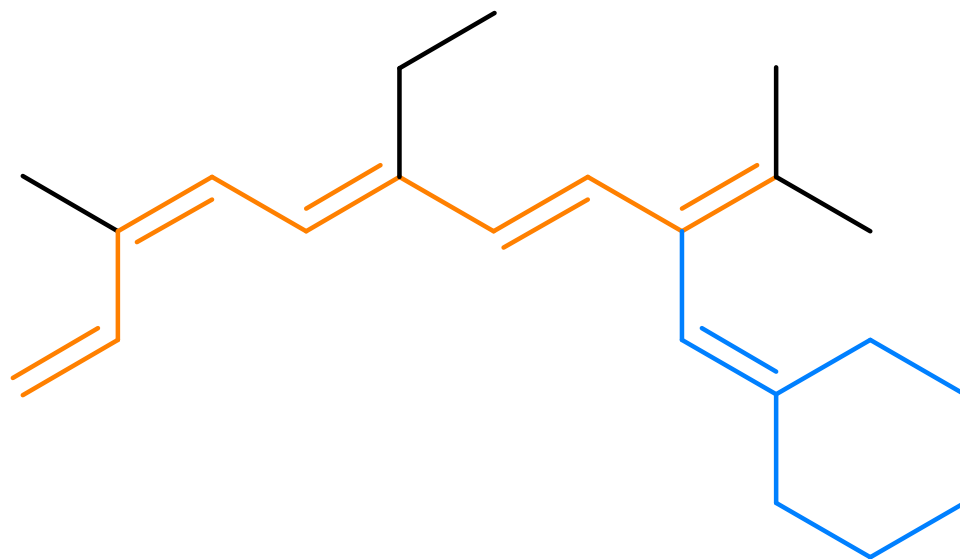
$$\lambda_{\max} (\text{nm}) = \mathbf{383 \text{ nm}}$$

$$\lambda_{\max} (\text{nm}) = \mathbf{A/B+C+D+Substituents}$$

$$\lambda_{\max} (\text{nm}) = 253+60+3(5)+[0+5+(6 \times 5)]$$

$$\lambda_{\max} (\text{nm}) = \mathbf{363 \text{ nm}}$$

Calculating λ_{\max}



$$\lambda_{\max} (\text{nm}) = 114 + 5S + n (48 - 1.7n) - 16.5 R_{\text{endo}} - 10 R_{\text{exo}}$$
$$\lambda_{\max} (\text{nm}) = 114 + 5 (4) + 5 [48 - (1.7 \times 5)] - 16.5 (0) - 10 (1)$$
$$\lambda_{\max} (\text{nm}) = 114 + 20 + 197.5 - 0 - 10$$
$$\lambda_{\max} (\text{nm}) = 321.5 \text{ nm}$$

Calculating λ_{\max}



β -carotene

$$\lambda_{\max} (\text{nm}) = 114 + 5S + n (48 - 1.7n) - 16.5 R_{\text{endo}} - 10 R_{\text{exo}}$$

$$\lambda_{\max} (\text{nm}) = 114 + 5 (10) + 11 [48 - (1.7 \times 11)] - 16.5 (2) - 10 (0)$$

$$\lambda_{\max} (\text{nm}) = 114 + 50 + 322.3 - 33 - 0$$

$$\lambda_{\max} (\text{nm}) = 453.3 \text{ nm}$$

Calculating λ_{\max}



Lycopene

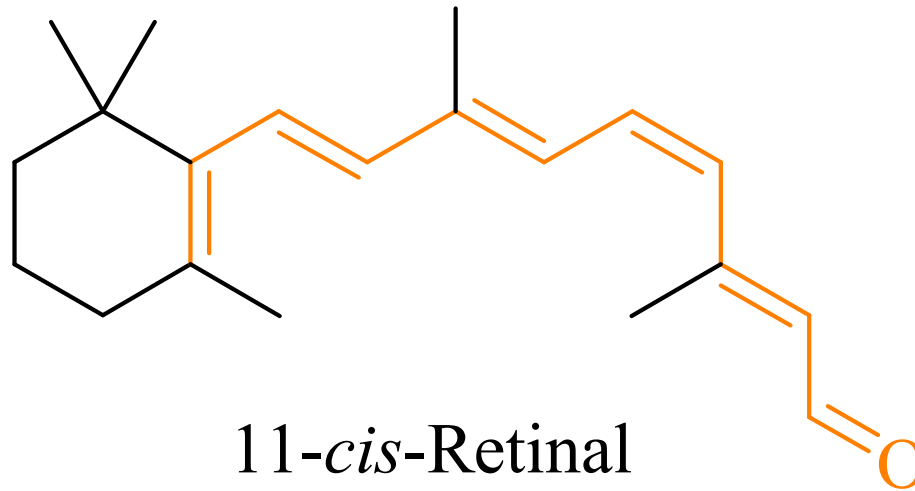
$$\lambda_{\max} (\text{nm}) = 114 + 5S + n (48 - 1.7n) - 16.5 R_{\text{endo}} - 10 R_{\text{exo}}$$

$$\lambda_{\max} (\text{nm}) = 114 + 5 (8) + 11 [48 - (1.7 \times 11)] - 16.5 (0) - 10 (0)$$

$$\lambda_{\max} (\text{nm}) = 114 + 40 + 322.3 - 0 - 0$$

$$\lambda_{\max} (\text{nm}) = 476.3 \text{ nm}$$

Calculating λ_{\max}



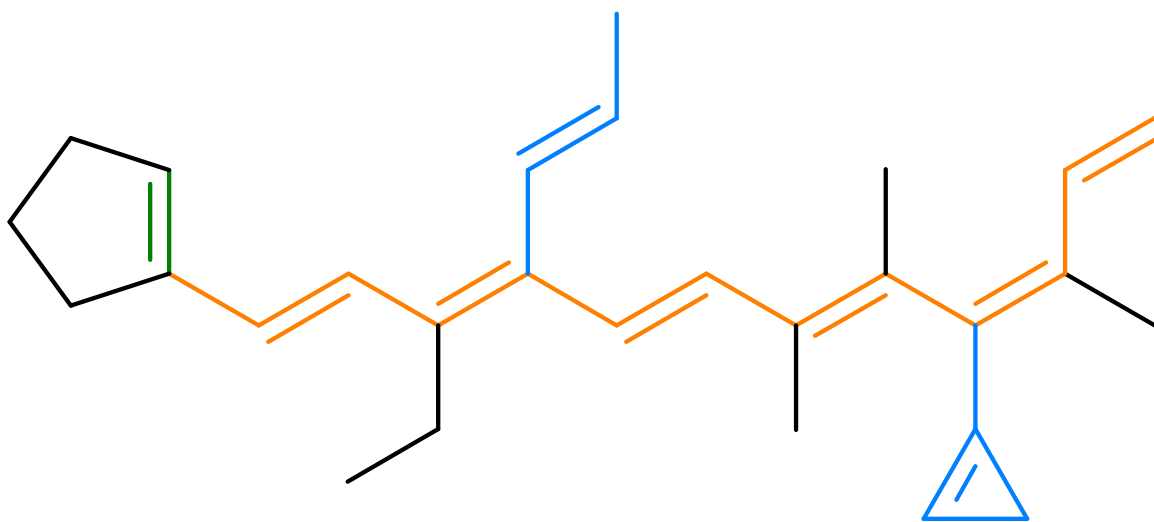
$$\lambda_{\max} (\text{nm}) = 114 + 5S + n (48 - 1.7n) - 16.5 R_{\text{endo}} - 10 R_{\text{exo}}$$

$$\lambda_{\max} (\text{nm}) = 114 + 5 (5) + 6 [48 - (1.7 \times 6)] - 16.5 (1) - 10 (0)$$

$$\lambda_{\max} (\text{nm}) = 114 + 25 + 210.3 - 16.5 - 0$$

$$\lambda_{\max} (\text{nm}) = 349.3 \text{ nm}$$

Calculating λ_{\max}



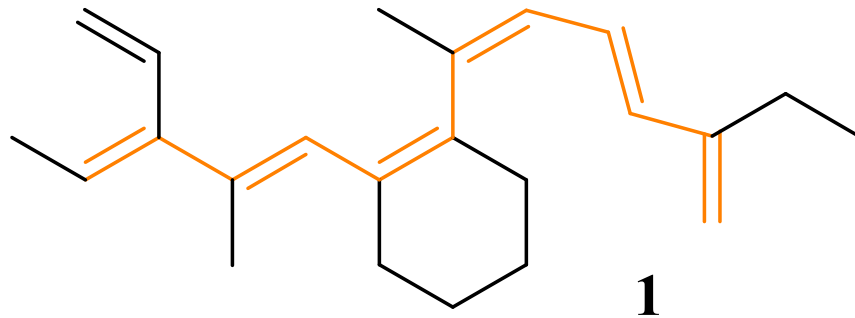
$$\lambda_{\max} (\text{nm}) = 114 + 5S + n (48 - 1.7n) - 16.5 R_{\text{endo}} - 10 R_{\text{exo}}$$

$$\lambda_{\max} (\text{nm}) = 114 + 5 (6) + 7 [48 - (1.7 \times 7)] - 16.5 (1) - 10 (2)$$

$$\lambda_{\max} (\text{nm}) = 114 + 30 + 252.7 - 16.5 - 20$$

$$\lambda_{\max} (\text{nm}) = 360.2 \text{ nm}$$

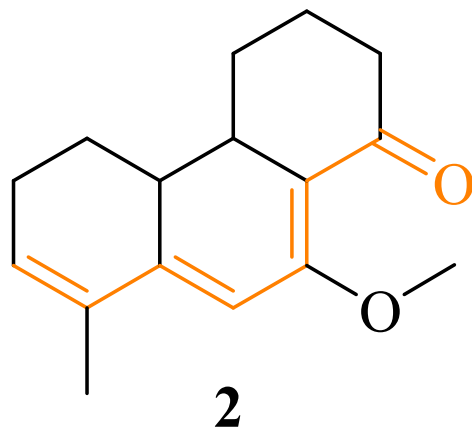
Calculating λ_{max}



$$\lambda_{max} = 114 + 5(6) + 6(48 - 1.7 \times 6) - 16.5 - 10$$

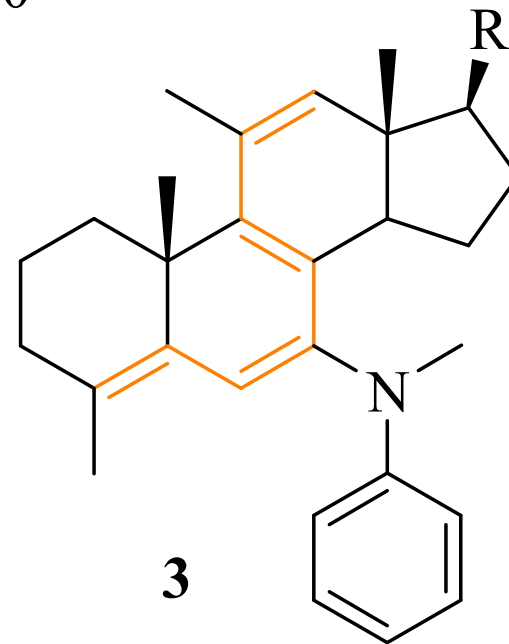
$$114 + 30 + 226.8 - 16.5 - 10$$

$$344.3 \text{ nm}$$



$$\lambda_{max} = 443 \text{ nm}$$

- 215 Base Value
- 39 Homoannular
- 60 2 (C=C) extension
- 10 Exocyclic C=C
- 25 Alkyl substituents
- 10 α -Alkyl group
- 30 β -OMe group
- 18 δ -Alkyl group
- 36 ω -Alkyl group



$$\lambda_{max} = 413 \text{ nm}$$

Crocus sativus (Saffron)

